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Supramolecular strategy to construct quantum dot-based sensors for detection of paraoxon

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ABSTRACT

The development of advanced tools for sensing specific materials remains an ongoing challenge. Detailed below is a new quantum dot (QD)-based sensor *via* supramolecular interactions, demonstrating a novel simplicity of design to obtain sensitive QDs while avoiding their covalent cross-linking. A simple label-free and turn-off method for the detection of paraoxon and its degradation products in aqueous media was proposed by using the fluorescent QD/surfactant/cyclodextrin supramolecular system. This nanocomposite was prepared from 3-mercaptopropionic acid-capped CdTe QDs coated with cetyltrimethylammonium bromide (CTAB) through electrostatic self-assembly. Further nanocomposite modification by β-cyclodextrin (β-CD), thanks to hydrophobic interaction between cetyl tails of surfactants and inner cavity of macrocycle contributed to an increase in emission intensity and stability in aqueous solution. The strong fluorescence of CdTe/CTAB/β-CD nanocomposite can be effectively quenched by the addition of paraoxon due to the host–guest complexation between β-CD cavity and paraoxon degradation product. The functionality of the paraoxon sensor was also tested with blood samples of paraoxon-poisoned rats ($1/2 \times LD_{50}$). These fluorescent nanocomposites were obtained by using the simple supramolecular method to coat QDs with surfactant–cyclodextrin shells. This coating strategy potentially offers common method for the functionalization of QDs and avoids time-consuming synthesis procedures.

1. Introduction

In recent years, much attention has been paid to the development of new functional systems based on the supramolecular chemistry approach [1]. For example, a bottom-up synthesis provides design methods of nanoscale systems with sensor applications [2]. Among these systems in the spotlight are fluorescent semiconductor nanocrystals, also known as quantum dots (QDs). Manufacturing methods of QDs using the bottom-up approach are essential in biological and medical fields [3]. Colloidal QDs are of particular interest because they are not rigidly bound to any matrix or substrate. As a result, it is possible to manipulate these QDs in the creation of composite materials or nanodevices. They can be embedded in a variety of matrices, planted on various surfaces, connected to other nanoparticles or molecules, and also used as building blocks for the creation of nanodevices and the fabrication of nanostructures based on self-assembly, photoinduced and template assembly of ordered structures with given optical parameters.

Conjugation or surface modification of colloidal QDs to make them water-soluble, stable, and functional is crucial for their applications and can be realized either covalently or non-covalently [4]. Such macrocycles as cyclodextrins, calixarenes, porphyrins, phthalocyanines, can be bound to the surface of QDs only by chemical synthesis methods [5–10]. In contrast, the supramolecular structures can be readily accessed using bottom-up synthesis as they utilize noncovalent interactions requiring fewer steps for modification. In a manner of employing noncovalent interactions instead of covalent bonding, sensory ensembles are built spontaneously from individual building blocks to form aggregates with the hope of achieving the specificity in recognition important for sensing [11]. Hence, for more effective performance, the molecules used for recognition purposes must exploit noncovalent interactions instead of covalent bonds.

Within the supramolecular approach, a key role is given to the macrocyclic scaffolds. Cyclodextrins, along with calixarenes, cryptands, crown ethers, and cucurbiturils, are macrocyclic compounds that have

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